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[3E]-3-Deoxy-3-*C*-ethoxycarbonylmethylene-1,2:5,6-di-*O*-isopropylidene- α -*D*-ribohexofuranose

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[3E]-3-Deoxy-3-C-ethoxycarbonylmethylene-1,2:5,6-di-O-isopropylidene- α -D-ribohexofuranoseAnthony Linden,^{a*} C. Kuan Lee^b
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Key indicators

Single-crystal X-ray study

T = 273 K

Mean $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$

R factor = 0.064

wR factor = 0.200

Data-to-parameter ratio = 7.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The furanoid sugar ring and the 1,2-*O*-isopropylidene ring of the title compound, $\text{C}_{16}\text{H}_{24}\text{O}_7$, have envelope conformations, while the 5,6-*O*-isopropylidene ring has a half-chair conformation.

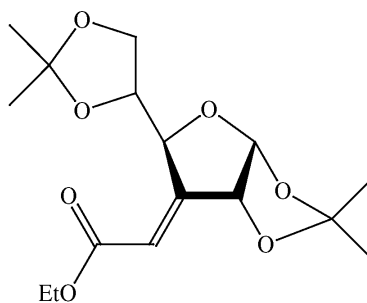
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Comment

Branched-chain sugars (Yoshimura, 1984) have been found as components of many antibiotics and other natural products which possess interesting biological activities. Many of these compounds have furopyran structures. Examples of these are azadiractin (Broughton *et al.*, 1986; Ley *et al.*, 1987) and miharamycin A and B (Seto *et al.*, 1983; Koul, 1984a). The former is an insect anti-feedant (Koul, 1984a,b; Rembold, 1984) isolated from the neem tree and the latter are active against rice blast disease caused by *Pyricularia oryzae* (Ley *et al.*, 1987). Our interest is to find convenient and efficient approaches to the synthesis of furopyran and related fused-ring systems from readily available sugars and their derivatives. As part of this programme, the title compound, (I), was synthesized and its structure determined.



(I)

Fig. 1 depicts the correct absolute configuration of (I), which was assigned to agree with the known chirality of D-glucose, from which (I) was synthesized. The molecule contains three five-membered rings which exhibit various conformations. The furanoid sugar ring has an envelope conformation puckered at C1, as indicated by the puckering parameter, $\varphi_2 = 222 (2)^\circ$ (Cremer & Pople, 1975). Atom C1 lies 0.295 (8) Å from the plane defined by C2, C3, C4 and O4. The 1,2-*O*-isopropylidene ring also has an envelope conformation [$\varphi_2 = 208 (2)^\circ$] with C1 lying 0.346 (8) Å from the plane through C10, O1, O2 and C2. The 5,6-*O*-isopropylidene ring has a half-chair conformation [$\varphi_2 = 93.0 (17)^\circ$] with C6 and O6 lying 0.173 (8) and $-0.260 (7)$ Å, respectively, from the plane defined by O5, C5 and C7.

The atomic displacement parameters for O6 and the adjacent methyl groups of the 5,6-*O*-isopropylidene ring are slightly enlarged, which suggests that the part of the ring containing O6 is quite flexible. However, there are no significant peaks of residual electron density in the vicinity of O6, so that the possibility of the ring having two different envelope conformations can be excluded. This effect has also been observed in the corresponding 3-*C*-ethoxycarbonylmethyl derivative (Linden *et al.*, 1996). The elongated atomic displacement ellipsoids for the ethyl group of the ester substituent also suggest that this group is disordered. However, the data quality did not enable a sensible model for the disorder to be developed. As an artefact of the untreated disorder, the bond lengths in this region of the molecule appear to be unduly short.

Experimental

Compound (I) was prepared according to the procedure of Rosenthal & Nguyen (1967). Suitable crystals were obtained by recrystallization from ether/petroleum ether at room temperature (m.p. 310–311 K).

Crystal data

$C_{16}H_{24}O_7$	$D_x = 1.257 \text{ Mg m}^{-3}$
$M_r = 328.36$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 23 reflections
$a = 5.929 (2) \text{ \AA}$	$\theta = 13.0\text{--}18.5^\circ$
$b = 14.133 (2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 10.3892 (12) \text{ \AA}$	$T = 273 (1) \text{ K}$
$\beta = 95.065 (16)^\circ$	Prism, colourless
$V = 867.2 (3) \text{ \AA}^3$	$0.38 \times 0.24 \times 0.15 \text{ mm}$
$Z = 2$	

Data collection

Rigaku AFC-5R diffractometer	$h = 0 \rightarrow 7$
ω - 2θ scans	$k = 0 \rightarrow 16$
1752 measured reflections	$l = -12 \rightarrow 12$
1588 independent reflections	3 standard reflections
891 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{\text{int}} = 0.018$	intensity decay: none
$\theta_{\text{max}} = 25.0^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1053P)^2 + 0.2323P]$
$R[F^2 > 2\sigma(F^2)] = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.200$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.47 \text{ e \AA}^{-3}$
1588 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
213 parameters	
H-atom parameters constrained	

Crystals of the title compound suffered thermal-shock damage when cooled to low temperatures and it was therefore necessary to record the data at 273 K. The crystals also diffracted quite weakly at this temperature, which lead to a paucity of reflections with significant intensities and a consequent decrease in the precision of the geometric parameters. The methyl H atoms were constrained to an ideal geometry with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but were allowed to rotate freely about the C–C bonds. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The absolute configuration could not be determined because of the absence of significant anomalous scatterers in the compound. The enantiomer used in the model was based on the known chirality of D-glucose, from which (I)

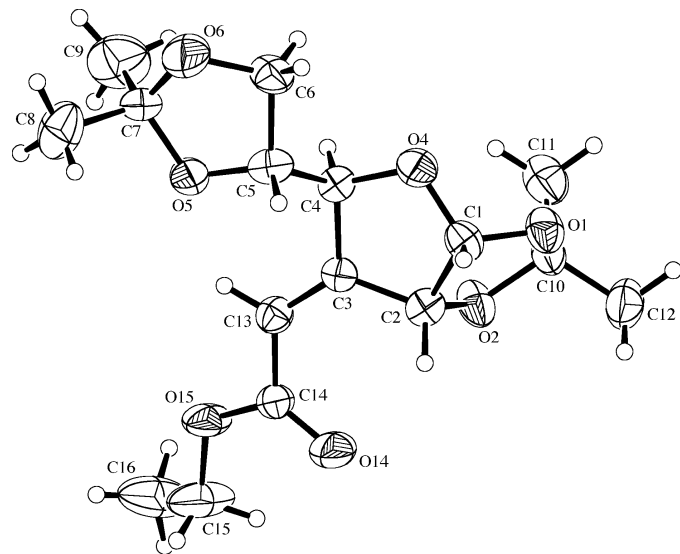


Figure 1

The molecular structure of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

was synthesized. Friedel pairs were merged before the final refinement.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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